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# SOLID PROPELLANT FLAMMABILITY INCLUD-ING IGNITABILITY AND COMBUSTION LIMITS

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**13. ABSTRACT**

Studies were directed at developing an understanding of mechanisms of propellants burning in air and of factors that control limits of burning so that one may rationalize choices of propellant formulation, charge configuration, process techniques, and special additives to reduce accidental ignition and burning of propellants in ambient air. Propellants were categorized in terms of convective, conductive, and radiative ignition data and in terms of burning rate and extinguishment limit data. The flammability of AP and HMX composite propellants is greatly increased by the presence of air; generally double base propellants are more flammable than the composite propellants, both in $N_2$ and air. Three types of additives for reducing flammability were evaluated: coolants (e.g., oxamide), char formers (e.g., phosphates), and flame inhibitors (e.g., halogen compounds). No practical success has been achieved with char formers and flame inhibitors. Significant improvements in the flammability limits have been achieved using coolants (at the 10% level) with composite propellants made from high decomposition-temperature ingredients (e.g., HMX and polyurethane).

1.

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| 14 KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Ignition | | | | | | |
| Flammability | | | | | | |
| Combustion | | | | | | |
| Caseless propellant | | | | | | |
| extinguishment limit | | | | | | |

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# BALLISTIC RESEARCH LABORATORIES

## REPORT NO. 1701

### MARCH 1974

## SOLID PROPELLANT FLAMMABILITY INCLUDING
## IGNITABILITY AND COMBUSTION LIMITS

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# GLOSSARY

| | |
|---|---|
| MTN or TMETN | trimethylol ethane trinitrate (metrial trinitrate) |
| TEGDN | triethylene glycol trinitrate |
| PNC | particulate nitrocellulose (typically 12.6%N) |
| PbSa | lead salicylate |
| CuSa | cupric salicylate |
| NG | nitroglycerine |
| HMX | $(CH_2NNO_2)_4$ |
| Phoschek-30 | ammonium polyphosphate $NH_4(PO_3H)_mNH_4$ |
| Oxamide | $(NH_2COCONH_2)$ |
| PU | polyurethane binder system |
| TAGN | triaminoguanidine nitrate |
| SEAP | self-extinguishing at atmospheric pressure |
| TCC/W | Wasatch Division of the Thiokol Chemical Corp. |
| EC | ethyl centralite (a stabilizer) |

# I. INTRODUCTION AND BACKGROUND

Accidental ignition of solid propellants in ambient air and the modification of solid propellants to reduce their susceptibility to accidental ignition were investigated analytically and experimentally. The susceptibility of solid propellants to accidental ignition in ambient air is a consequence of an interplay among factors inherent in the propellant make-up and circumstantial elements of the immediate environment. At the heart of this interplay is the oxygen in the air which greatly modifies the ignition and burning characteristics of the propellant. However, the extent of the influence of atmospheric oxygen is very dependent on items such as wind velocity, propellant geometry, propellant container geometry, and propellant formulation.

Figure 1 is a schematic drawing showing a representation of a two-stage flame which results when propellant is burned in air. The reactions can be considered to occur in three zones as shown in Figure 1. Under conditions of slow heating and slow burning, an appreciable fraction of the heat release may occur in the condensed phase. Adjacent to the surface is a premixed flame (i.e., a self-flame) which under high pressure conditions does not depend on an external oxygen supply. The reaction products from the self-flame undergo further reaction when they come in contact with the atmospheric air. The result is a diffusion flame (i.e., the second flame) between the products of the self-flame and the surrounding air. At pressures near one atmosphere, this second flame increases burning rate and flammability. In most situations, air is supplied to the second flame by a combination of several processes including natural convection, (i.e., buoyancy forces), forced convection (e.g., wind), and currents set up because of the unsteadiness of the flame.

The goal of the study being reported here is to develop understanding of mechanisms of propellants burning in air and of factors that control the limits of burning so that one may rationalize the choice of propellant formulation, charge configuration, process techniques, and special additives to reduce flammability. (This study was not intended as a propellant development program; several propulsion companies have been awarded contracts to develop propellants resistant to accidental ignition and burning.)

The emphasis of this report is on:

(a) How the burning of propellant combustion products with air affects propellant ignition, burning rate, and flammability limits, and

(b) How additives intended to reduce flammability affect the flammability limits.
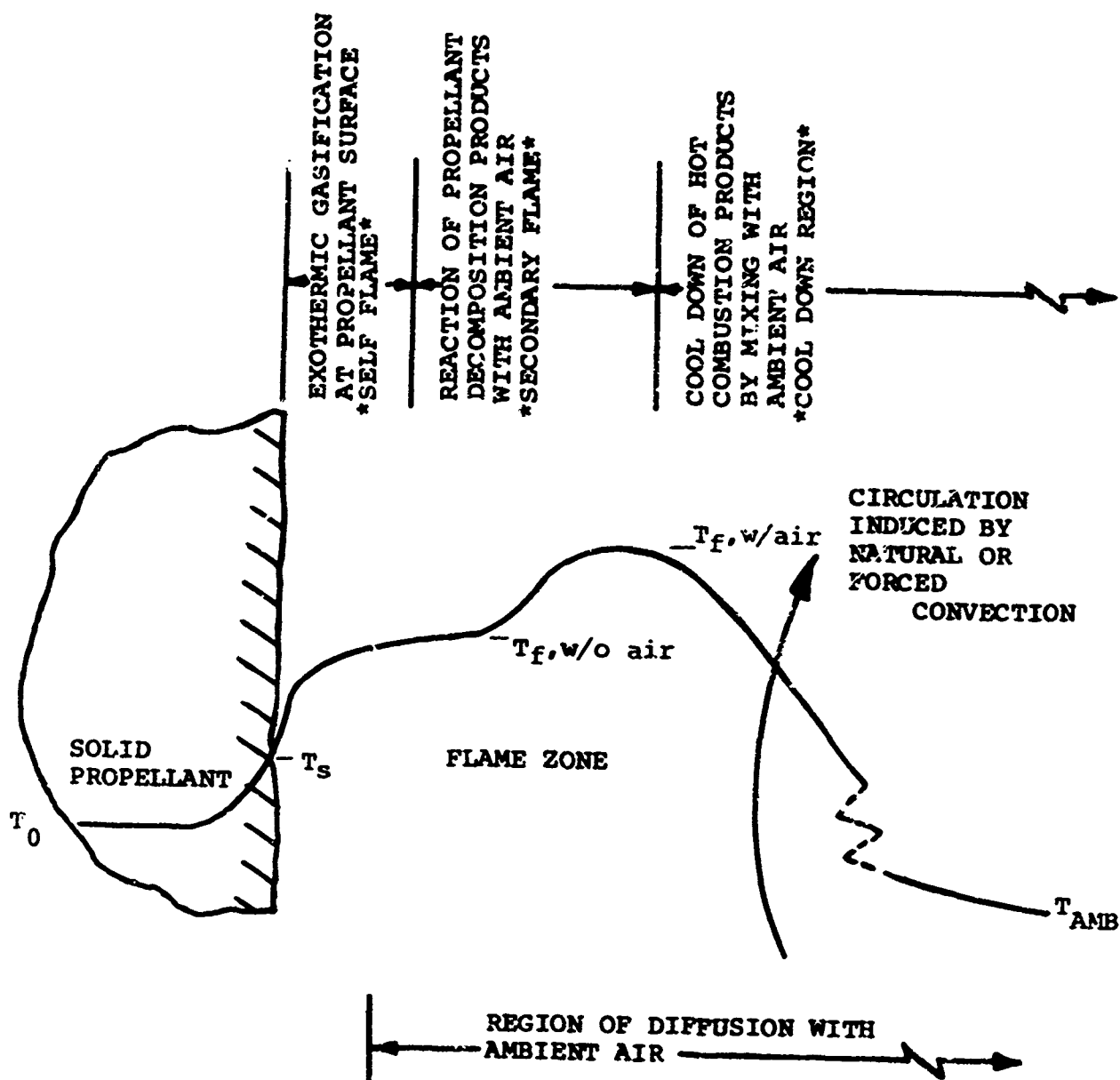
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Fig. 1  Schematic drawing showing combustion zones of
propellant burning in atmospheric oxygen
(Greatly simplified one dimensional section
from a multi-dimensional configuration)

In general terms, propellant flammability is a measure of three component processes: ignitability, flame retention, and flame spreading. Ignitability here refers to the ability of the propellant to yield (sooner or later) sustained exothermic reactions under the influence of an external heat source. Flame retention refers to two factors: whether the conditions at the time subsequent to thermal runaway are within the combustion limits for steady burning and whether the flame is sufficiently stable to survive rapid removal of the external heat source (if removal occurs). Flame spreading refers to subsequent ignition of propellant regions adjacent to that first ignited, as influenced by both the external heat source and the heat supplied by the existing flame. All of these component processes are subject to significant alterations by ambient oxygen and by propellant formulation variations (e.g., oxidizer percentage, oxidizer type, use of coolants and flame inhibitors).

Various studies of the normal, low pressure burning limits have been made.[1-4]* The ultimate causes are usually taken to be radiative heat loss from the propellant surface and incomplete reactions corresponding to low pressure. Different classes of propellants show widely varying limits. Ammonium perchlorate (AP) composites generally have sub-atmospheric burning limits which, for certain binder types, may extend as low as 1/200 atm (in $N_2$); double base propellant flames tend to be much less tenacious in this respect and have exhibited limits above one atmosphere (in $N_2$). Indeed, AP composite propellants have been specially formulated to extend this limit to above three atmospheres.[3,4] The key factor here is the balance between heat loss and heat generation in the immediate neighborhood of the propellant surface. This balance can clearly be tipped in the direction of persisting combustion if oxygen can approach the surface and react strongly with the emitted gases; in this view both the oxygen supply rate and its reactability with the gases dictate its influence on flammability limits.

A.  Definitions and Criteria Associated with Nonflammability

We have found it useful to categorize and critique several of the requirements and criteria for nonflammable propellants. The requirements for the sought after, nonflammable propellant are summarized as follows:

1.  Shall not ignite or if ignited shall not retain flame (Note: two separate possibilities) under ordinary ambient conditions: P = 1 atm; $T_{amb}$ = up to 140F; 21% $O_2$; possible winds, possible radiation.

2.  Shall burn readily at elevated pressures in hot, inert atmospheres (combustion products) in chamber, after ignition and produce normal ballistics.

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*References are listed on page 38

3. Other requirements not directly relevant to principles of nonflammability: smokeless, no chamber residues, high energy resist premature ignition (cook-off), etc.

A suitable criterion of nonflammability must account for the relative importance of three component processes: ignitibility, flame spreading, and flame retention. The following criteria which cover each of three component processes are followed by an assessment in terms of the overall objectives of this study:

1. The sought-after propellant is very difficult to ignite. This means that "ignition temperature" is very high, or that required ignition energy is very large. Evaluation of this criterion: severe exposure conditions will initiate sustained burning.

2. Even if the propellant is ignited, it resists flame spreading. Evaluation of this criterion: if the propellant can be ignited, the flame will eventually spread, especially in a breeze or in combustion-generated air flow in a confined space.

3. Even if the propellant is ignited, the flame will die out promptly after the ignition source is removed. The element here is non-retention of flame under free atmosphere conditions. This criterion is the most acceptable goal in terms of the objectives of this study: if the propellant will refuse to continue burning, then it is immaterial how intense an ignition source was used or whether conditions favorable for flame spreading may exist -- the flame will go out. (This is self-extinguishment at atmospheric pressure, "SEAP".)

When attention is focused on Criterion 3, then we examine propellants already burning steadily and ask whether they will go out. For example, we ask whether the flame will generate an internal impedance element that may upset the steady-state energy balance, or whether the presumed steady flame is indeed stable under possible small perturbations (non-steady perturbation theory). Following this criterion studies of ignition transients (start of the flame) and the study of flame spreading rates are set aside. Instead, emphasis is placed on the nonretention of the flame under atmospheric conditions.

There are two types of flame zone/condensed phase interactions leading to self-extinguishment:

1. Failure to satisfy the steady-state energy balance at the burning surface (or elsewhere) due to heat loss or incomplete combustion.

2. Failure to satisfy stability conditions under small perturbations, when burning under constant ambient conditions.

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In principle, combustion limits or flame retention limits exist for all
solid propellants. In some cases, they are of type 1 extinguishment, and
in at least two propellants the type 2 extinguishment has been unambiguously
identified. The aim of adding char-formers, coolants, and/or rate
retardants (to be discussed later) is to move the extinguishment
boundaries above 1 atm pressure at the 140°F ambient temperature.

## B. Effect of Air/Propellant Products Diffusion Flame

Equilibrium thermodynamic flame temperatures were calculated[5] to
estimate the temperature of the second flame (Figure 2) of two propellant
types. Reburning the HMX composite propellant products greatly increases
$T_f$ (~800°K) while the $T_f$ of the double base propellant increases
slightly. An examination of the $H_2O$ and $CO_2$ concentration and the amount
of air required to achieve the maximum $T_f$ indicates that double base
propellant is a more nearly balanced system; thus, flammability of the
double base propellant is less likely to be affected by ambient air
(this will be emphasized in subsequent sections).

Another realization in the search for a low flammability propellant
is that the very modifications that tend to decrease the intensity of
the self flame increase the relative heat feedback contributions of the
second flame. As the self flame decreases, the burning rate decreases.
This in turn decreases the blowing away from the surface and permits
the ambient oxygen to diffuse closer to the surface, bringing the
second flame closer to the surface. This is illustrated by the analytical
results of Figure 3 in which the burning rate is decreased by lowering
the initial temperature of the propellant. Note that below 300°K in $N_2$
the burning rate decreases rapidly, while in air the heat feedback from
the second flame has a dominant role. Furthermore at the higher burning
rates corresponding to the higher temperatures, the ambient air has a
diminishing effect on burning rate because of the previously explained
blowing away (from the surface) of the second flame. The calculations
of Figure 3 were performed using the analytical model which will be
described in Reference 6.

## II. APPROACHES TO REDUCING FLAMMABILITY

Fire retardants which have been used by the textile and plastics
industries in various commerical applications can be classified into
three categories[7] according to the mechanism by which they act: (a)
coolants which absorb a large amount of energy near the burning surface,
(b) flame inhibitors which suppress the gas phase reactions near the
burning surface, and (c) compounds which promote the formation of
carbonaceous surface layers that block heat feedback from the flame to
the surface. In addition, binders and oxidizers with high decomposition
and ignition temperatures have been found to reduce flammability.
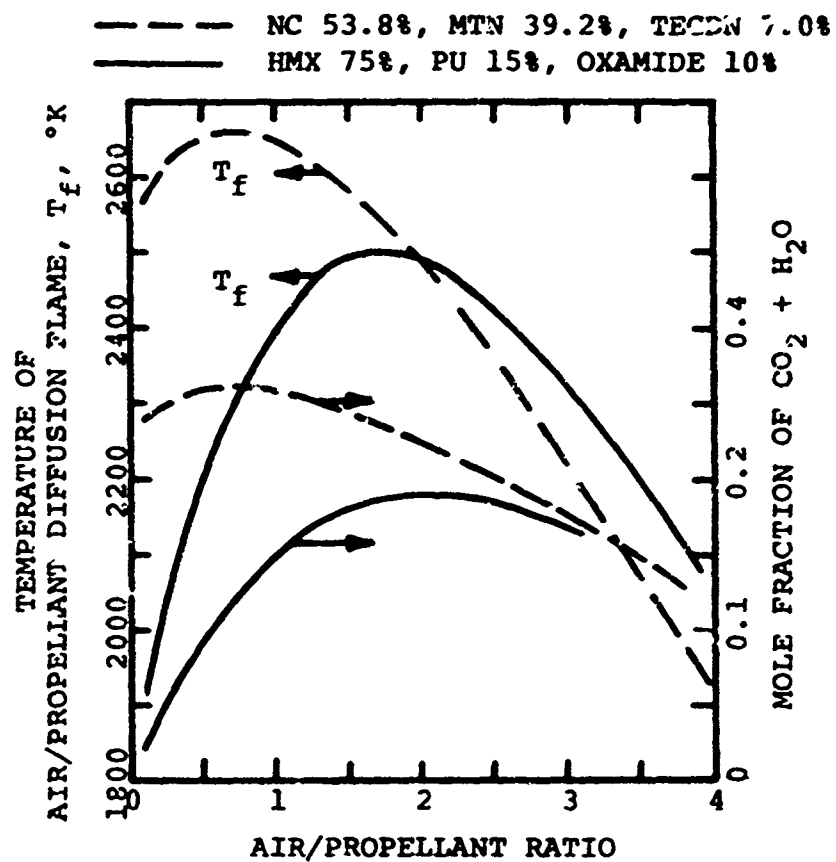
Fig. 2  NC propellants interact less with
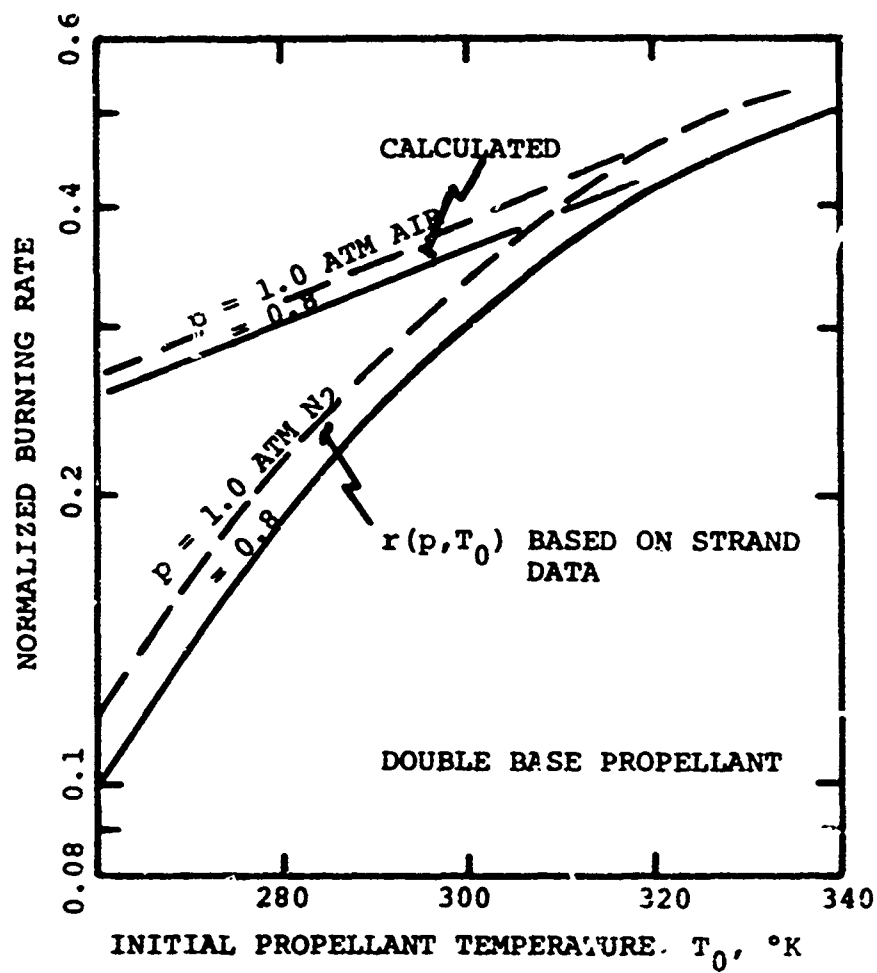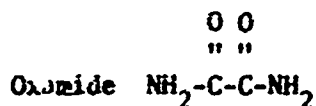        air than HMX composite propellants

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Fig. 3 As the basic burning rate decreases the heating from the air/propellant products diffusion flame becomes more prominent.

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The following are examples of compounds which can be considered as coolants when added to propellants:

$$\text{Oxamide} \quad NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

Ammonium Oxalate $(NH_4)_2 C_2O_4$
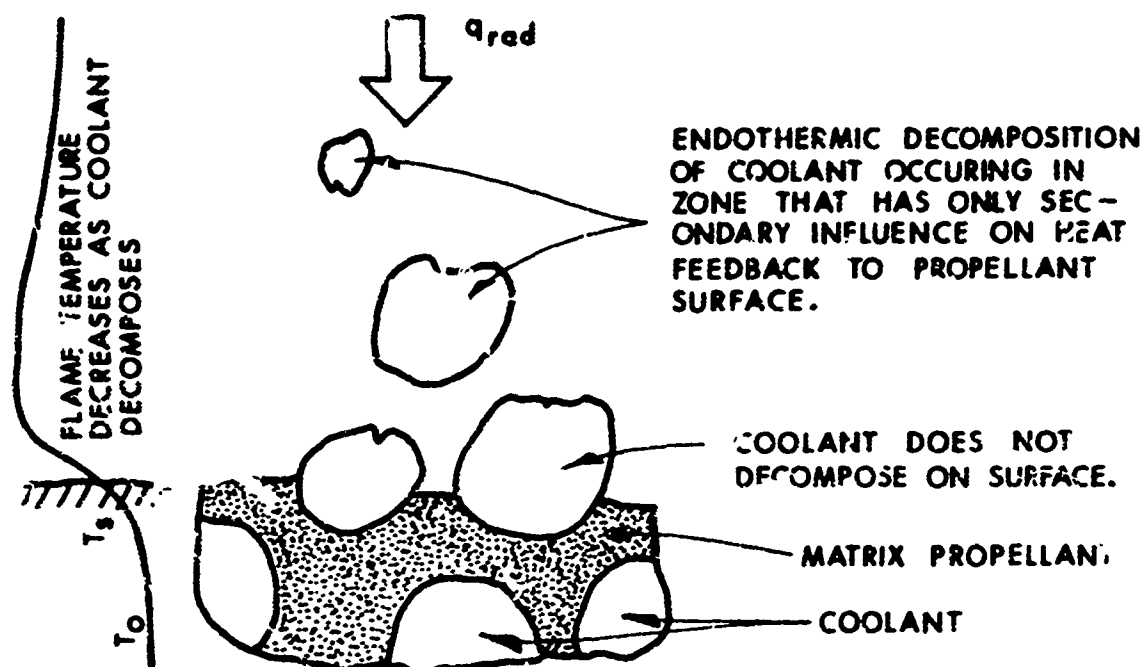
Hydroxylammonium Oxalate $(NH_3OH_2) C_2O_4$

To realize fully the flammability reducing capacity of a coolant added to propellant as a powder, the coolant must endothermically decompose before it leaves the surface of the matrix propellant. This is the premise which will be considered in this section. Figure 4 illustrates two situations: (a) the undesirable situation of a coolant decomposing after it leaves the propellant surface, and (b) the desirable situation of the coolant endothermically decomposing at the propellant surface. The difference between the surface temperature of the matrix propellant and the decomposition temperature of the coolant is the important consideration in terms of the above premise. The temperature of decomposition at slow heating rates is a secondary consideration, since the low temperature decompositions that occur during slow heating are not indicative of the higher condensed phase temperatures that accompany rapid ignition and self-sustaining combustion.

The hoped for fire retardant mechanism of various halogen compounds is considered to be a flame inhibition action by means of radical trapping in the vapor phase. For example, consider the free radical reaction of a bromine compound:

$$RBr + H\cdot \rightarrow HBr + R \quad . \tag{1}$$

which removes a very active species $H\cdot$ , and replaces it by a less reactive species R. It should be noted that while such flame inhibitors have the desired affect of decreasing the flame spreading rates[8] they do not greatly alter (at high pressure) the energy released by the burning propellant.

Several phosphorus containing compounds have been identified as promoting surface char layers.[7] As the parent material burns, these phosporous compounds react to yield long chain carbon compounds and eventually a char layer. As this char layer develops it was hypothesized that it would tend to insulate the surface from the heat feedback from the flame and to isolate the surface reaction zone from atmospheric oxygen. During the early stages of burning, the char layer should

$q_{rad}$

ENDOTHERMIC DECOMPOSITION OF COOLANT OCCURING IN ZONE THAT HAS ONLY SEC- ONDARY INFLUENCE ON HEAT FEEDBACK TO PROPELLANT SURFACE.

FLAME TEMPERATURE DECREASES AS COOLANT DECOMPOSES

COOLANT DOES NOT DECOMPOSE ON SURFACE.

MATRIX PROPELLANT

COOLANT

$T_s$

$T_o$

a) Coolant decomposition temperature higher than surface temperature of basic propellant. Thus the endothermic decomposition does not appreciably affect the zone that influences ignitability and burning rate.

ENDOTHERMIC DECCMPOSI- TION OF COOLANT OCCURS AT PROPELLANT SURFACE.

b) Coolant decomposition temperature is lower than the surface temperature. Thus, the endothermic decomposition occurs in a zone where it has a profound influence on ignitability and burning rate.

Fig. 4  Conditions which determine whether a coolant will be effective in reducing propellant flammability.

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(following the hypothesis) begin to insulate the surface from the second flame. If the char formation is successful as a fire retardant, heat feedback from the second flame to the propellant should become progressively weaker until the effects of ambient air become unimportant. It was contemplated that a propellant which will self-extinguish in $N_2$ would also self-extinguish behind a sufficiently thick char layer.

One of the purposes of the experimental studies was to evaluate the hypothesized effects of the three types of flammability reducing additives.

### III. TESTS USED TO EVALUATE FLAMMABILITY

In this paper reference will be made to ignition data obtained from three types of ignition sources: (a) radiation using a tungsten filament lamp (heat flux up to 10 cal/sec-$cm^2$), (b) forced convection using an acetylene flame (1.7 cm long from a No. 00 Micro-torch nozzle), and (c) hot plate (or conduction) using an electrically heated copper plate.

The hot-plate ignition apparatus was designed to subject the propellant sample to a square-wave exposure by a (nearly) constant temperature copper plate. As shown in Figure 5, before the exposure interval, the propellant sample is isolated from radiative and natural convective heating emanating from the hot plate for a predetermined time and then it is returned to the position shown in Figure 5. The test is a go/no-go test. A more complete description of the apparatus is given in Reference 9.

Impact and radiation ignition apparatus for evaluating the flammability and sensitivity of propellants under ambient conditions were also developed by Shock Hydrodynamics, Inc.[10]

Another test for assessing the effectiveness of flammability reducing methods is to measure burning rate as a function of pressure and to determine the pressure ($p_i$) below which ignited propellant will self-extinguish. The propellant can usually be ignited (at least temporarily) by creating a local hot spot. Thus a measure of success would be to increase $p_i$. If $p_i$ can be made greater than one atmosphere, then the propellant satisfies criterion c. The tests were carried out in a specially fabricated chamber (ID = 26 cm and height = 53 cm) which maintains a prescribed air pressure and introduces fresh air to prevent oxygen depletion during the test. The propellant sample is a 0.635 cm cube mounted on a needle so as to be exposed on all sides. Ignition of the sample is achieved by a carefully controlled pyrogen-type igniter which engulfs the entire sample in flame. In this paper, mass burning rates (i.e., the average mass consumption rate of the cube) will be reported since they are more repeatable than the present linear burning rate data.
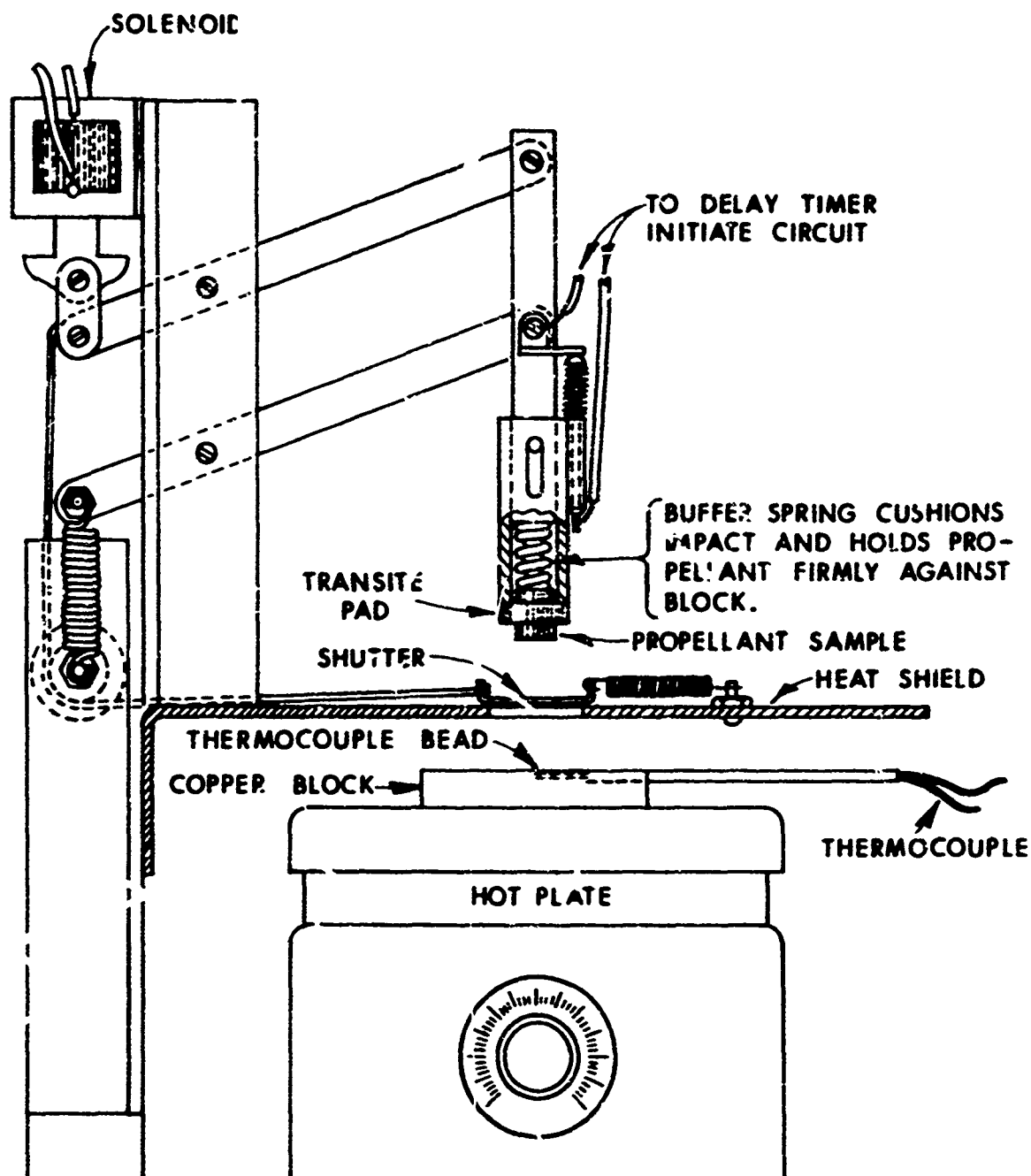
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Fig. 5  Diagram of hot plate ignition test
apparatus

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# IV. EXPERIMENTAL RESULTS

The scope of the laboratory evaluation of the approaches to reducing flammability are summarized in Table I. The columns on the left of the table show the four modes of retarding combustion. The experiments were carried out with three classes of propellants. The double base propellants and the HMX composite propellants are of broad interest to the Army. However, the halogen additives, AP composite propellants, and the propellants using flourocarbon binders are not suitable for many of the Army applications since their combustion products are particularly corrosive. We studied these formulations because they helped us to understand mechanisms which may lead to reduced flammability using ingredients which do not produce corrosive products. Table I indicates which of the five standard laboratory measurements have been obtained. Those that are circled will be discussed in this report.

In several evaluations, additives were incorporated to the extent that the energy level or physical properties of the resulting propellants were unsatisfactory. Such propellants were useful in establishing the combustion trends produced by the additives and should not be considered as candidate propellants.

One of the more useful observations on the effectiveness of additives to reduce flammability is the effect of the additive on the pressure at which combustion cannot be sustained (i.e., the pressure of the deflagration limit, $p_i$). Table II is a summary of such data for a variety of propellants burning either in air or in $N_2$. Note that the $p_i$ values of double base propellants (1055, 1056, and 1090) are affected only slightly by the atmosphere of the chamber. Conversely, the $p_i$ values of the HMX composite propellants (which have very high $p_i$ values in $N_2$) are greatly affected when the combustion occurs in air rather than $N_2$. Part of the explanation for the marked difference between the double base and HMX composite propellants is revealed by examining Figure 2 which shows that HMX composite propellant self-flame products are much more reactive with air than the double base self-flame products.

Another useful observation is the effect of the additives on burning rate as a function of pressure. Figure 6 summarizes the r vs p and $p_i$ data for five propellants containing HMX. As expected the burning rates of the HMX/PU/oxamide propellants decrease as the percentage of oxamide is increased.

The results of hot plate ignition tests (Figure 7) produced three conclusions: (a) double base propellants are very susceptible to conductive ignition, (b) the HMX/polyurethane composite propellants are relatively resistant to conductive ignition, and (c) oxamide appears to be very effective as a coolant for all classes of propellants tested.

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Table I.

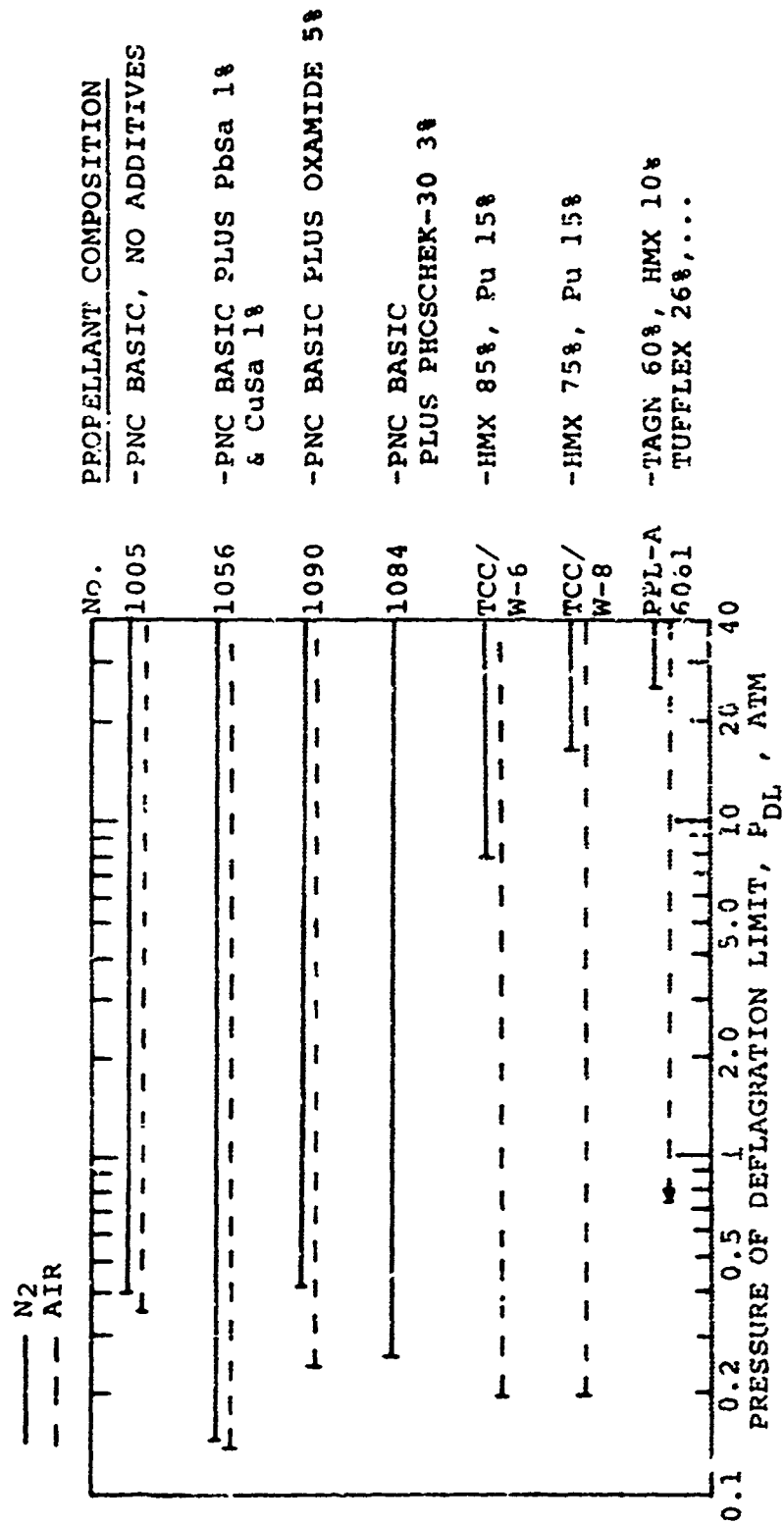Scope of Laboratory Evaluation of Candidate Approaches

| MODE OF RETARDING COMBUSTION | EXAMPLE | PROPELLANT CLASS | | |
|---|---|---|---|---|
| | | DOUBLE BASE, NC/MTM | AP COMPOSITE | HMX COMPOSITE |
| HIGH DECOMPOSITION TEMPATURE INGRED. | HMX vs NC, TEFLONvsPU | | | RAD FLA HP / Pi m |
| SURFACE COOLANTS | OXAMIDE | RAD FLA HP / Pi m | RAL FLA HP | RAD FLA HP / Pi m |
| SURFACE BLOCKAGE, CHAR FORMERS | PHOSPHATES | RAD FLA HP / Pi m | RAD Pi / m | RAD FLA |
| FLAME INHIBITORS | BrX | Pi m | Pi m | Pi m |

IGNITION TESTS: RADIATION -RAD, FLAME -FLA, HOT PLATE -HP

SELF-EXTINGUISH. TESTS:

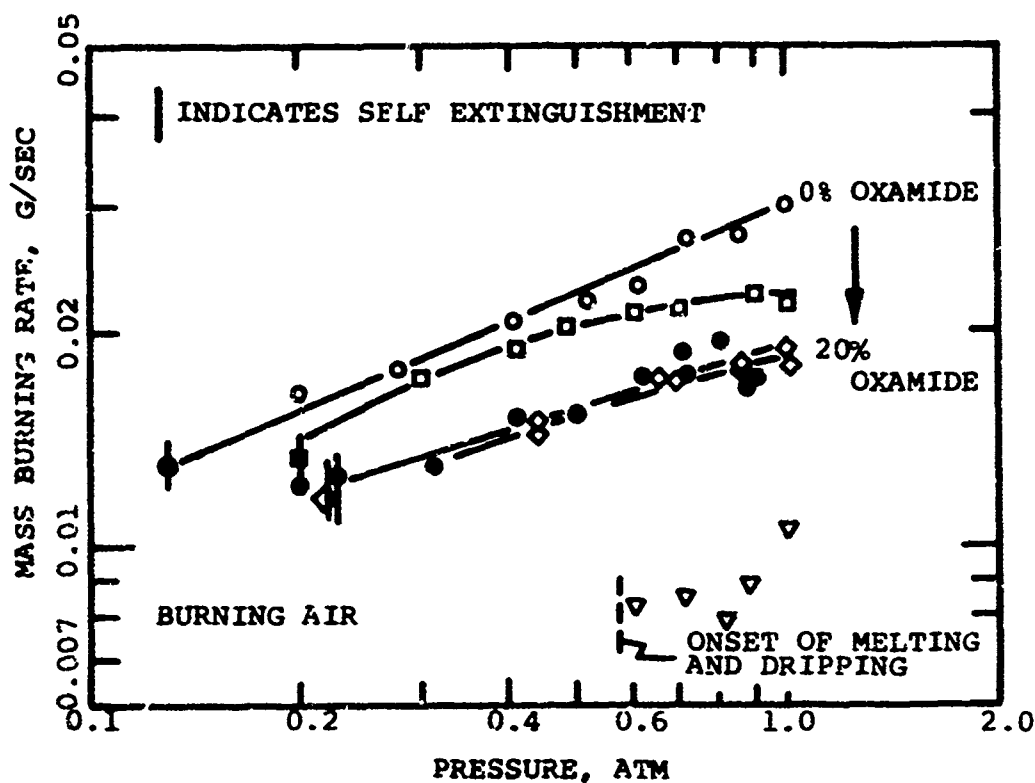LOWEST IGNITION PRESS.-$P_i$, m vs $P_{air}$

For conciseness, only the tests with a ◯ around them are discussed in the text.

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Table II.

Deflagration Pressures in Air are Below 1 atm
for HMX Composite and NC Formulations



| No. | PROPELLANT COMPOSITION |
|-----|------------------------|
| 1005 | -PNC BASIC, NO ADDITIVES |
| 1056 | -PNC BASIC PLUS PbSa 1% & CuSa 1% |
| 1090 | -PNC BASIC PLUS OXAMIDE 5% |
| 1084 | -PNC BASIC PLUS PHOSCHEK-30 3% |
| TCC/W-6 | -HMX 85%, Pu 15% |
| TCC/W-8 | -HMX 75%, Pu 15% |
| PPL-A 60.1 | -TAGN 60%, HMX 10% TUFFLEX 26%,... |

N₂
— — AIR

PRESSURE OF DEFLAGRATION LIMIT, $P_{DL}$ , ATM

0.1   0.2   0.5   1   2.0   5.0   10   20   40

Fig. 6 Measured mass burning rates and pressures of self-
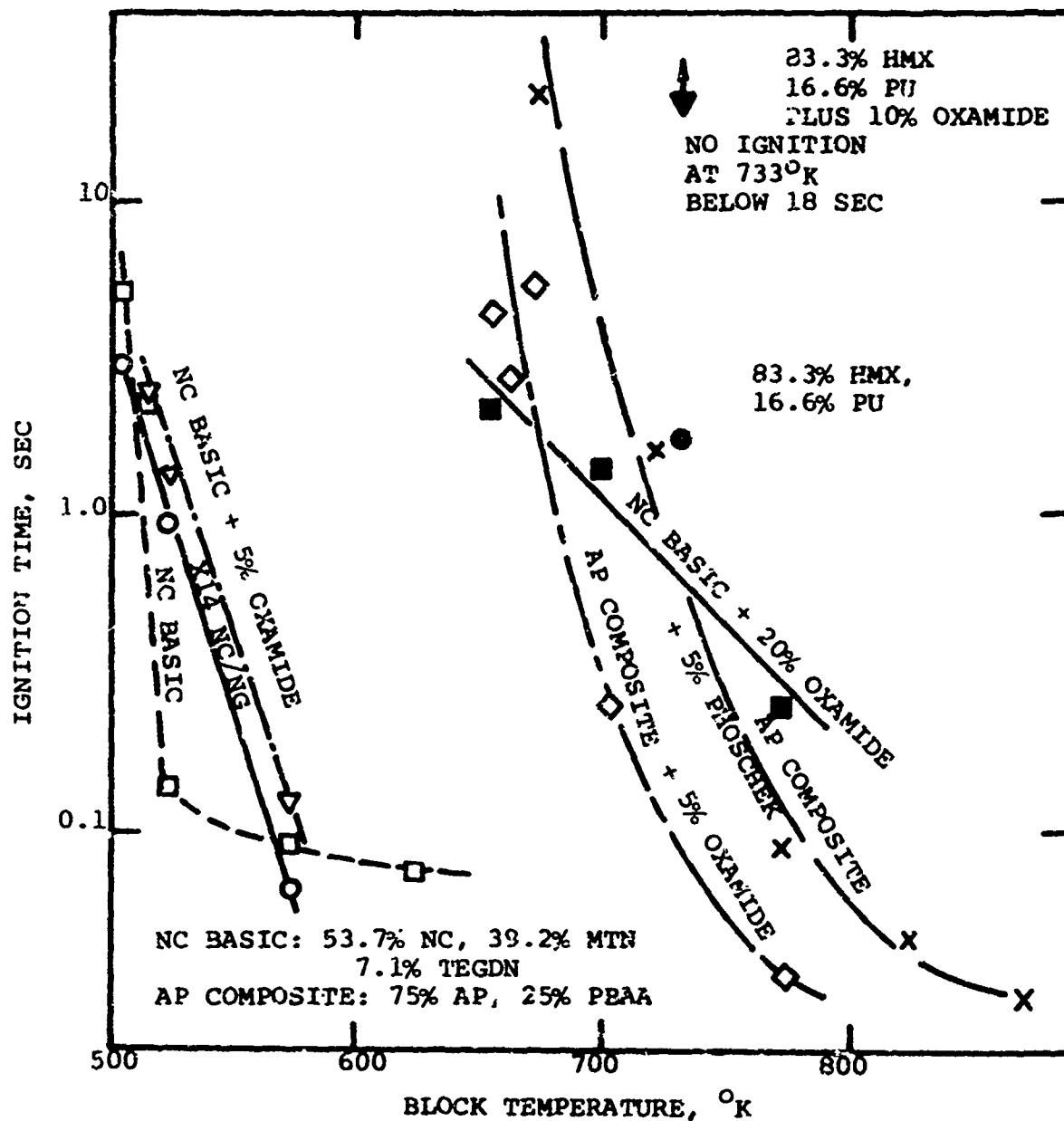extinguishment for propellants burning in air.

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Fig. 7  Hot plate ignition data showing that unmodified
double base propellants are relatively easy to
ignite and that the HMX/PU composite propellants
are very resistant to ignition

Note that the HMX/polyurethane composite propellant with 10% oxamide withstood 733°K for 18 seconds without igniting. The fact that oxamide is effective in suppressing conductive ignition and not radiative and convective ignition of the nitrocellulose propellants may result from the oxamide decomposing on the hot plate adjacent to propellant surface rather than in the distended flame zone of the nitrocellulose based propellant.

When oxamide is added to the double base propellants (which have very low surface temperatures), the following are observed:
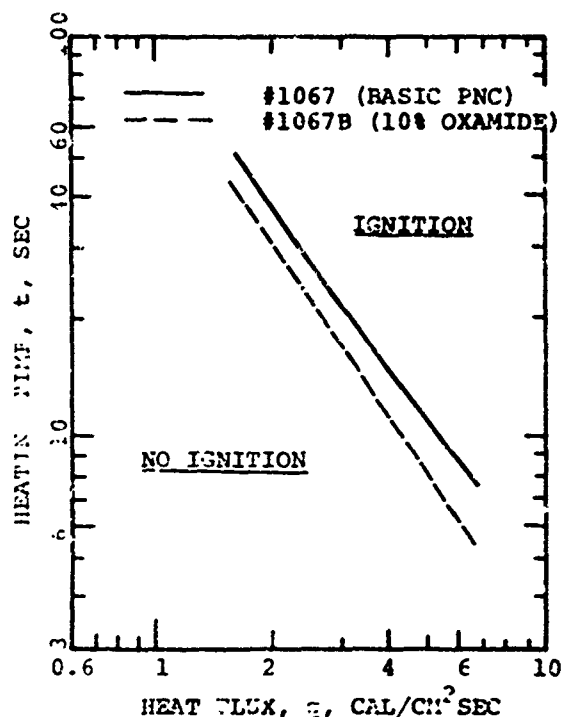
(a) Oxamide does not appreciably affect $p_i$ in $N_2$ (Table II).

(b) Oxamide decreases the flame temperature gradient (as measured by $7.5\mu$ thermocouples) but has no clearly discernible effect on the propellant surface temperature.

(c) Oxamide does not make the propellant more difficult to ignite (Figure 8a). Also, the results of the ignition experiment are similar when it is carried out in $N_2$ (see Figure 8b).

The proposed explanation of all three observations is the same: since the surface temperature of the matrix propellant is lower than the decomposition temperature of oxamide, the endothermic decomposition of the oxamide is not centered at the propellant surface. However, there is a slight contribution from the oxamide (in the flame zone), i.e., since at the 5% level, oxamide produces a 20% reduction in burning rate.
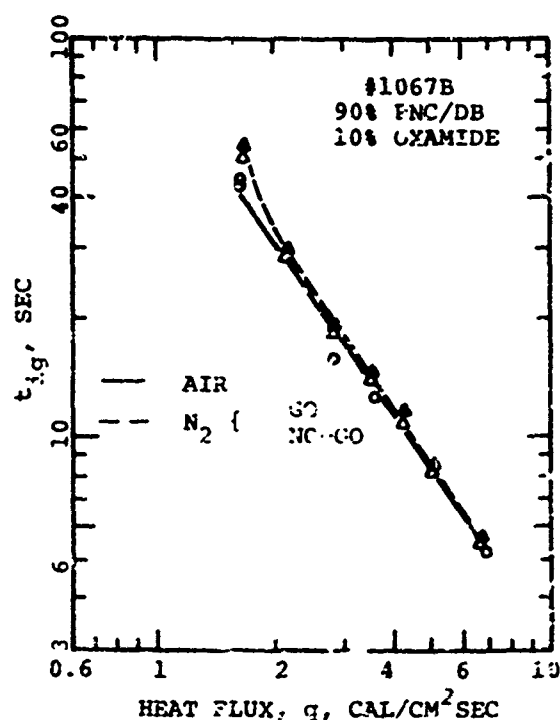
To further explore the effect of additives whose decomposition temperatures are higher than the surface temperature of the matrix propellant, ammonium perchlorate (AP) was added to the basic NC double base propellant. AP is known to have a higher surface temperature than NC double base propellants. AP (even though it is an oxidizer) does not affect appreciably the ignition limit of the NC double base propellant.

The ignition tests of AP composite propellants revealed that adding oxamide has no appreciable effect on the ignition boundaries. Again this suggests that even though the surface temperatures of the AP composite propellants are higher than the surface temperatures of the NC double base propellants, the decomposition temperature of the oxamide is sufficiently high that it does not decompose on the surface of the AP composite propellants.
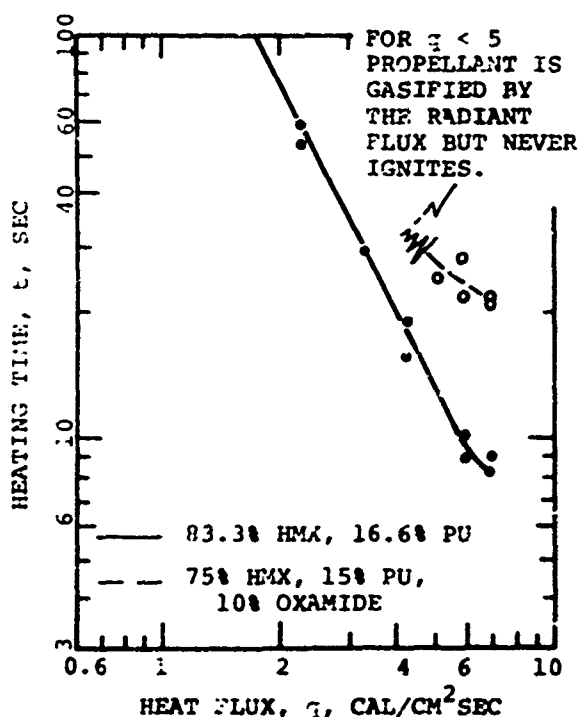
Finally, the ignition data (see Figure 8c) for the HMX/PU propellants support the premise that the surface temperature of the matrix propellant must be relatively high for the coolant to function as a flammability suppressant. As shown in Figure 8c, oxamide has a profound influence on the ignition characteristics. Indeed, for radiant heat fluxes less
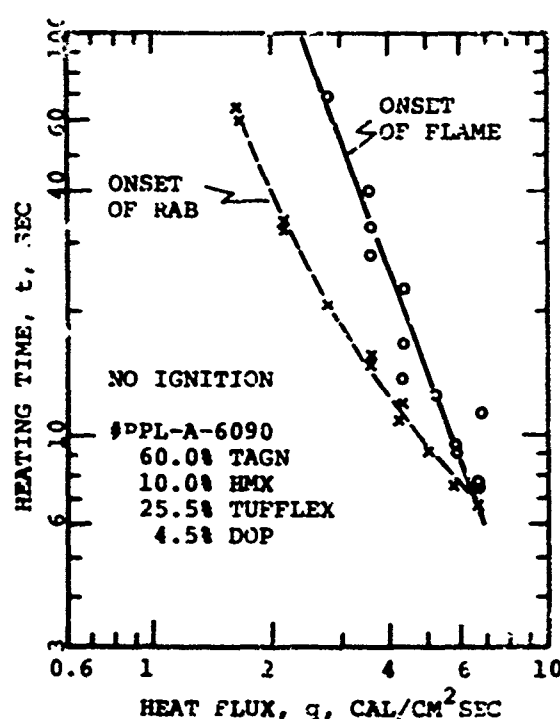
29

a)  Oxamide added to basic PNC/DB propellant showing that oxamide does not decrease ignitability.

b)  Ignition limit of PNC/DB propellant with 10% oxamide (in $N_2$ and air) showing that air does not alter ignitability.

c)  Data showing marked decrease in ignitability when 10% oxamide is added to HMX propellant TCC/W-5.

d)  Data for propellant #PPL-A-6090 showing marked difference between onset of radiative assisted burning (RAB) and ignition time.

Fig. 8  Ignition data obtained using the radiation source at 1 atm showing conditions for which coolants are effective

than 5 cal/sec-$cm^2$ the propellant containing 10% oxamide (TCC/W-4) is not ignited by radiation. The data of Reference 11 show that the surface temperature of the HMX composite propellants is about 1050°K. This is higher than the surface temperature of either the AP composite (700 to 900°K, Reference 12) or NC double base propellant (about 500°K, Reference 13). However, it must be noted that when the propellant is gasified and not ignited, the gases that emanate from the propellant surface are easily ignited by an open flame. The extent of this preignition gasification is shown in Figure 8d.

Figure 9 is a typical result that shows that an excessive amount of an additive (in this case $(NH_4)_2$ $HPO_4$, which is a char former when used with commercial plastics) is required to make $p_i$ approach one atm. Even with large amounts (10 to 20%) the $(NH_4)_2$ $HPO_4$ is ineffective as a char former and is probably acting as a diluent and coolant. Note that the large particle size is more effective, indicating that the burning rate suppressing reaction is probably occurring at the surface.

Figures 10 and 11 show that large amounts of a flame inhibitor (ethylene dibromide) are ineffective when used with either AP composite or double base propellants. The effects of adding six different bromine compounds to the propellants have been evaluated without any indication of reduced flammability. Thus, additives which are known to reduce the flame speeds of gases[8] and the flammability of commercial (nonenergetic) plastics[9] are not effective in reducing the flammability of propellants.

## V. RELATING PROPELLANT FLAMMABILITY HAZARDS TO CONVENTIONAL HAZARDS

To obtain insights into how the hazards associated with low flammability propellants compare to the hazards of more conventional materials, a conventional ball powder protected by a thin (0.025 cm) brass sheet and samples of cloth were subjected to the same ignition conditions as propellant samples. A comparison of the ignition times for cloth (Table III) with the ignition times for several propellants, reveals that the cloth samples ignite more easily than many of the propellants. Systematic testing demonstrated that because of the high thermal conductivity of brass it offers little protection to the propellant. Indeed, the brass protected ball powder ignited more easily than the unprotected propellant containing 75% HMX.

The last two compositions on Table III are materials which are intended to be used as outer layers on the main propellant charge. Since these outer layers make up a small percentage of the total charge weight, greater improvements in flammability achieved by sacrificing some of the energy in outer layers produce relatively small penalties in the energy of the overall charge. Note that both of these outer layer materials self-extinguish when the acetylene flame is removed.
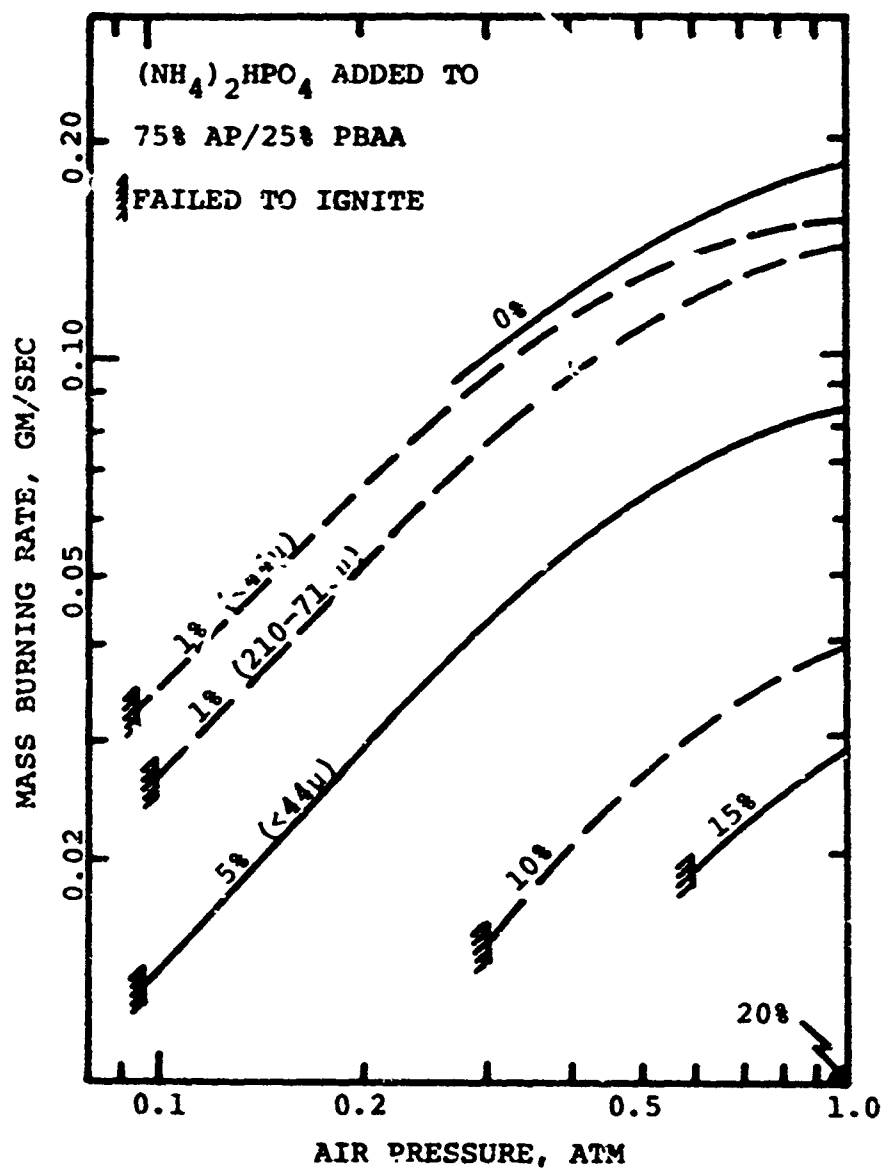
31

Fig. 9 Decrease of ignitability and burning
       rate of AP composite with increased
       phosphate loading.

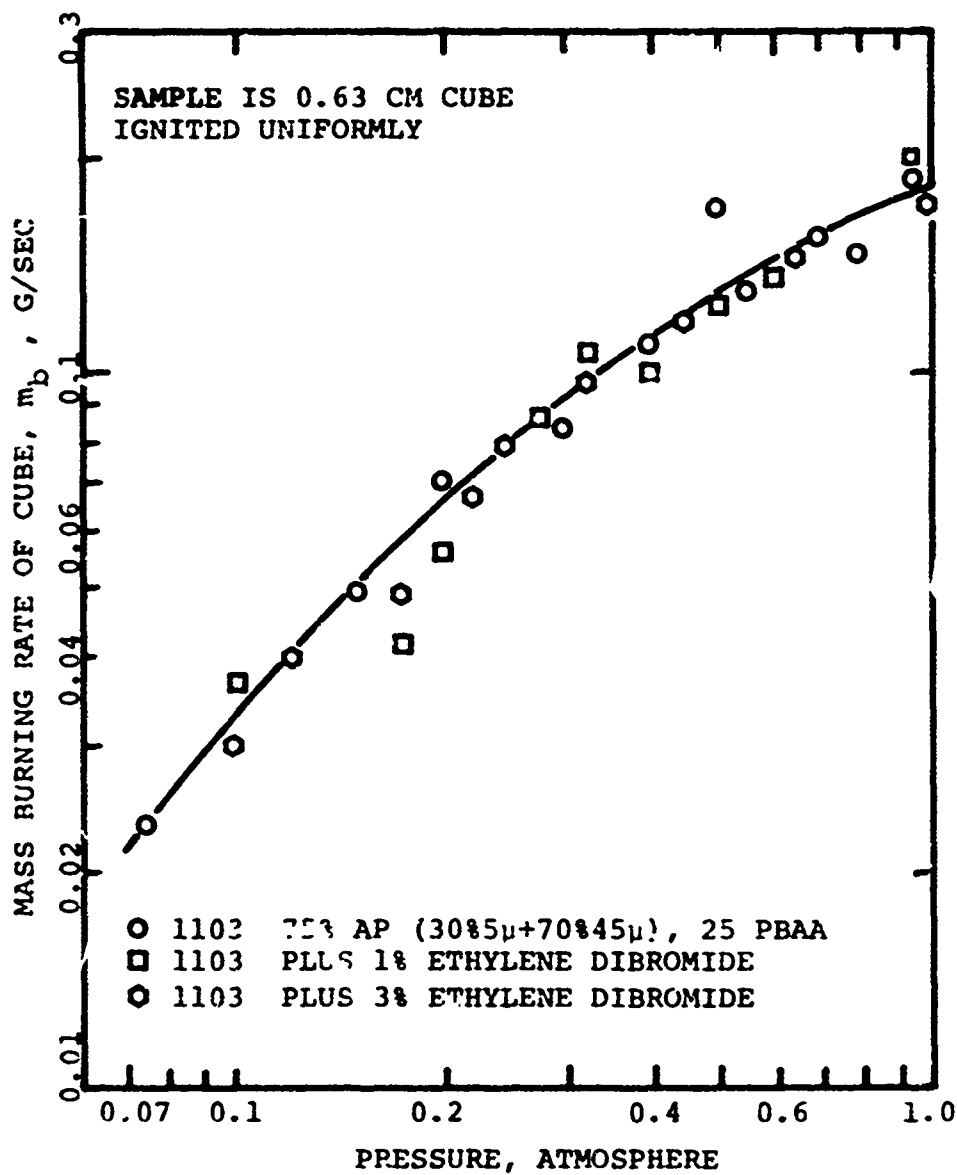Fig. 10 Burning rate versus pressure of AP/PBAA composite propellant modified with ethylene dibromide showing that ethylene dibromide does not affect the burning rate characteristics in the low pressure range.
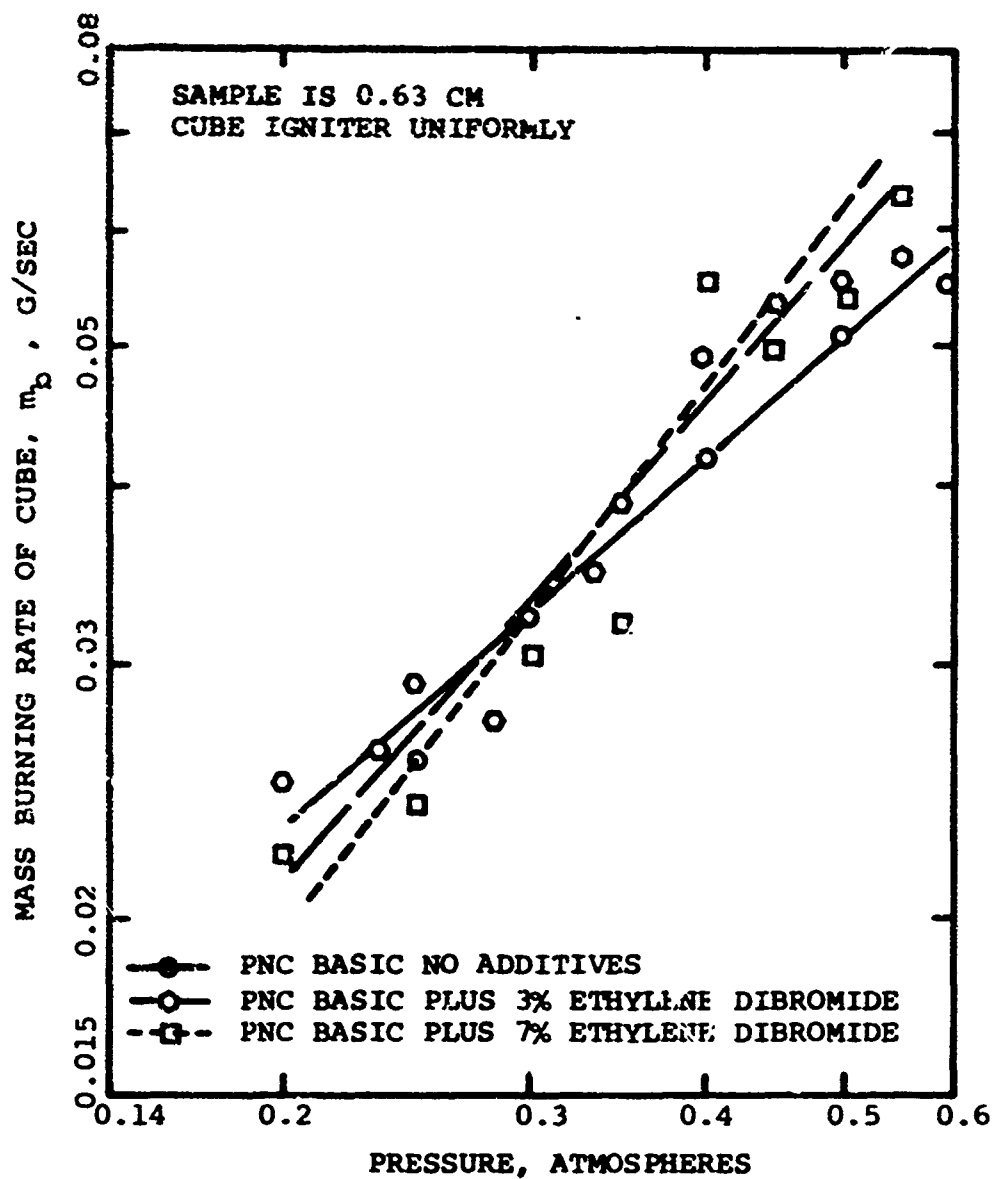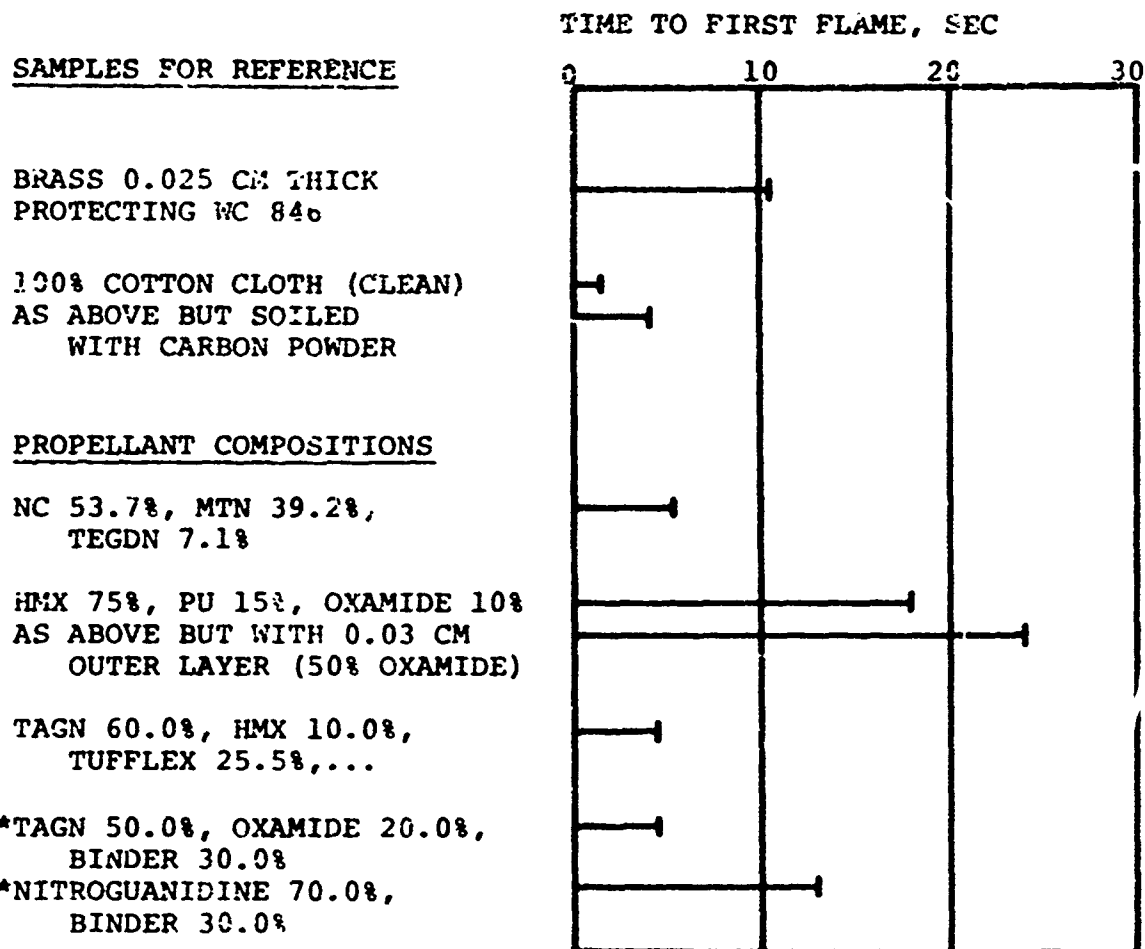
33

Fig. 11  Burning rate versus pressure of nitrocellulose
propellant modified with ethylene dibromide showing
that ethylene dibromide does not result in a useful
self-extinguishment point.

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## Table III.

**Several Propellants and Outer Layer Materials are
More Difficult to Ignite than Conventional Items**

--- HEATING SOURCE IS ACETYLENE FLAME 1.7 CM LONG ---

TIME TO FIRST FLAME, SEC

SAMPLES FOR REFERENCE

BRASS 0.025 CM THICK
PROTECTING WC 846

100% COTTON CLOTH (CLEAN)
AS ABOVE BUT SOILED
  WITH CARBON POWDER

PROPELLANT COMPOSITIONS

NC 53.7%, MTN 39.2%,
  TEGDN 7.1%

HMX 75%, PU 15%, OXAMIDE 10%
AS ABOVE BUT WITH 0.03 CM
  OUTER LAYER (50% OXAMIDE)

TAGN 60.0%, HMX 10.0%,
  TUFFLEX 25.5%,...

*TAGN 50.0%, OXAMIDE 20.0%,
  BINDER 30.0%
*NITROGUANIDINE 70.0%,
  BINDER 30.0%



*SELF-EXTINGUISHES WHEN ACETYLENE FLAME IS REMOVED.
NOTE:   The last two propellants are outer layer materials
        which are intended to protect a main propellant
        charge from accidental ignition and to be consumed
        in the chamber under operating conditions.

The results of Table III should be a source of encouragement since they indicate that ignition energy requirements of the low flammability propellants do not differ greatly from those of several conventional items.

## VI. CONCLUSIONS

Achieving a self-extinguishing, high energy propellant is a goal yet to be achieved. However, lower energy materials suitable for use as an outer-layer protective coating (which is consumed as an energetic material under the desired high pressure operating conditions) appear to be promising. Two of the conventional methods of reducing flammability, flame inhibitors and char formers, have been explored well beyond the range of practical limits and found to be ineffective when used with propellants.

The use of oxamide with the high decomposition temperature HMX/polyurethane composite propellants is effective in reducing flammability. The ignition limits of these propellants is well above the ignition limits of conventional clothing materials and ball powder propellants protected by a brass case.

## VII. FUTURE WORK

To date, a large part of the flammability investigations being conducted throughout the country have been directed at finding additives that would, when used in small amounts, make either nitrocellulose propellants or nitramine composite propellants self-extinguish at atmospheric pressure. The break through of finding such additives is preferred solution. However, it is now apparent that the usual fire retardants are not effective when used with self-oxidizing, high energy materials. Accordingly, to achieve the ultimate goals of the program, attention is being directed at obtaining an understanding of how the propellant decomposition processes that produce oxidizing species can be inhibited. Thus, a more detailed knowledge of the chemistry is required. Several concurrent approaches are underway. Precision gas sampling techniques are being developed to determine how the intermediate combustion products are affected by additives, which have the potential of inhibiting flame development. A more comprehensive mathematical model that accounts for the interplay among the surface, self-flame, and air/propellant combustion products flame zone is being applied to understand how suppressing the reactions in one (or more) of the zones can lead to self-extinguishment.

The fact that self-extinguishment is observed at 0.3 atmospheres of air tells us that the sought after physical effect exists. The task is to move the self-extinguishment boundary from 0.3 to 1.2 atmospheres of air.

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The work to date has indicated that a self-extinguishment limit
must be defined with respect to some limit on thermal abuse. For
example, any high energy material will burn if heated to a sufficiently
high temperature over a prescribed time. Thus, attention is being
directed at the task of developing tests for ranking the relative
hazards of propellants. The tests must take into account the applications
for which the propellants are intended and the packaging that will be
used in the field.

## ACKNOWLEDGMENT

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